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Interpretation of direct methanol fuel cell electrolyte properties using non-traditional length-scale parameters

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ABSTRACT

Numerous sulfonated polymer electrolyte membranes (PEMs) have been developed for direct methanol fuel cells (DMFCs) during the last decade. An analysis for DMFC PEMs obtained from the literature data and structural information is presented based on non-traditional length scale parameters. The analysis presented highlights specific differences in chemical composition between PEMs including perfluorinated sulfonic acids, hydrocarbon-based and polymers having specific interactions. Differences in cross-linked, homopolymer-like, random and multi-block polymer architectures are also discussed. The analysis presented gives important insight into molecular design aspects of sulfonated PEMs for DMFCs.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising energy conversion devices for portable power sources. One of the major research thrusts for DMFC development is the investigation of novel high performance polymer electrolyte membranes (PEMs) having a combination of high proton conductivity and low methanol permeability [1]. Extensive efforts have been made in different directions aimed at PEMs with desirable properties for DMFC applications in the last decade [2]. Most literature data reported key properties of PEMs benchmarked against Nafion® or a control hydrocarbon (HC)-based PEM. These reports generally focus on a single family of PEMs with very few reports that compare properties across a wide range of DMFC PEMs [3,4]. This work goes beyond prior reports by focusing on systematic analysis across the spectrum of PEMs.

Unlike PEMs used in H₂/air fuel cells, where a single key property (i.e. proton conductivity) has been the primary emphasis, PEMs for DMFCs have also been investigated with a strong emphasis on methanol permeability. Selectivity, which is defined as the ratio of proton conductivity to methanol permeability, has been suggested as a single key property of PEMs for DMFCs to compare

one polymer versus another [5]. A limitation of selectivity as a general gauge of DMFC PEMs is the requirement of a minimum conductivity necessary for effective operation of the DMFC, regardless of how low the methanol permeability is [2]. This minimum conductivity is related to the fact that the PEM itself has a minimum attainable thickness to achieve low cell resistance. Selectivity also fails to account for issues of mechanical/chemical robustness or the ability to be fabricated into high performance MEAs. Therefore, selectivity serves only as a screening tool for potential DMFC PEMs. Nonetheless, comparing properties of a wide range of PEMs is extremely beneficial since (i) it helps to better the understanding of structure–property relationships of PEMs, leading to accelerated development of advanced PEMs and (ii) it provides accurate information on the current state-of-the-art PEMs for DMFC developers, facilitating faster comparative investigation and ultimately, commercialization.

Recently, we reported a new length scale parameter, percent conducting volume (PCV) to better analyze and represent electrochemical properties of PEMs [6]. This proposed parameter arose from the belief that the use of mass-based parameters (most commonly used for these comparisons) are of limited value in evaluating transport properties across the wide range of PEMs, because PEMs may have significantly different densities and transport properties that occur over length scales more appropriately represented by volume measurements. One of the biggest advantages of using PCV is that this parameter removes

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Table 1
Molar volume increments of selected groups [7].

Groups	V_a (298) (cm ³ /mol)	Groups	V_a (298) (cm ³ /mol)
–H	5.5		32.5
–F	9.12		18.72
16.37		73.3
23.7		5.28
–CN	19.85		65.5
–CH3	21.87		69
–CH(C6H5)	84.16		112
–CH(CN)	30.7		6.88
–CHF–	20.0		20.22
–C(CH3)2	49.0		26.56
–C(CH3)(C6H5)–	100.5
17.3		
–O– (al.)	8.5		
–O– (ar.)	8.0		
–CF3	34.08
25.76		
N _{ar} (pyrid)	8.32		
–SO ₃ H	40.5		

the discrepancy of transport properties derived from differences between mass and volume normalized properties and more accurately reflects molecular structural effects in simpler and clearer terms. In particular, it takes into account the large density differences between most HC-based and perfluorinated sulfonic acid (PFSA) PEMs and allows them to be compared on a more appropriate basis. While density information on PEMs is not commonly reported, particularly as a function of hydration, PCV can be calculated from just molecular structure and hydration number (λ). The easy accessibility of PCV has an obvious advantage over other length scale parameters such as volume based IEC, which typically require additional measurements, thus allowing the possibility of a comparative evaluation of a wide range of PEMs that have been already reported without the need to obtain additional information.

In a previous paper, we demonstrated a conductivity analysis of multiple PEMs for fuel cell operation under low RH conditions using the PCV parameter. It concluded that sulfonated PEMs having highly localized (maximum phase contrast) (e.g. PFSA) and/or highly continuous hydrophilic phase domains (e.g. multi-block copolymers) had better proton conductivity at low RH conditions [6]. In the present paper, it is of interest to analyze a range of structurally different PEMs using the PCV parameter to provide a better understanding of structure–property relationships for DMFC applications. In order to accomplish this in a comprehensive way, a variety of sulfonated PEMs that have been reported in the literature are categorized based on molecular composition and polymer architecture. Then, proton conductivity, methanol permeability and selectivity of each class of PEMs are analyzed as a function of PCV to draw a trend. Finally some details of molecular structural effects are discussed based on the analysis. The ultimate purpose of this paper is to provide a general molecular design aspect of DMFC

PEMs without suggesting specific polymers and to guide research strategy for advanced DMFC PEMs.

2. Methods

The PCV value of each polymer is calculated from molar volume per charge (MVC) and λ . MVC is an estimate of equivalent volume (cm³ per ionomer or the mol. equiv. of acid groups) based on the summation of molar volume subunits rather than true volume measurements (Table 1 shows the molar volume increments of selected groups that are used in our calculations [7]):

$$MVC = \sum_i n_i V_i$$

where V_i is the volumetric contribution of the i th structural group that appears n_i times per charge.

MVC in hydrated state ($MVC_{(WET)}$) can be calculated from the MVC and λ .

$$MVC_{(WET)} = MVC + V_{H_2O} \cdot \lambda$$

where V_{H_2O} is the molar volume of water, 18 cm³ mol^{−1}.

PCV is defined as the ratio of the volume of the aqueous (hydrophilic) phase per acid site to an estimate of the volume of the hydrated membrane per acid site:

$$PCV = \frac{V_{H_2O} \cdot \lambda}{MVC_{(WET)}}$$

3. Results and discussion

3.1. Polymer classification and PCV calculation

Numerous PEMs and their properties for DMFC applications have been reported over the past 20 years or more. We limited our survey to ~600 PEM articles published after 2004 in order to focus on more recent developments in the field. From these articles, we selected only those for which molecular structural information, ion exchange capacity (IEC), water uptake, proton conductivity and methanol permeability were available. Over 200 PEMs from 46 independent papers matched these criteria [8–53]. The selected PEMs were then arbitrarily categorized based on their molecular composition into 4 classes: (i) PFSA, (ii) partially fluorinated, (iii) HC-based, and (iv) functional. PFSA include perfluorinated polymers with different equivalent weights (EWs). Partially fluorinated PEMs include partially fluorinated hydrocarbon or polymer blends including PFSA without the presence of specific functional groups. HC-based PEMs include non-fluorinated polymers in the absence of specific functional groups that interact with sulfonic acid or water molecules. Sulfonated polyaromatics derived from polyethers, polysulfones, polyketones, or polystyrene and sulfonated heterocyclics such as polyimides are classified into this category. HC-based PEMs are sub-categorized into (i) cross-linked, (ii) homo, (iii) random and (iv) graft/block (co)polymers for the purposes of further discussion. Functional PEMs include polymers or polymer blends containing basic moieties such as imidazole or amine, or other polar groups such as nitrile and phosphine oxide. These functional groups in PEMs have specific interactions that include acid–base, dipole–dipole or hydrogen bonding interactions based on their interaction with sulfonic acid groups and/or water.

MVC and PCV values were calculated as described in Section 2. For example, MVC and PCV of a sulfonated poly(ketone) having a chemical structure below and $\lambda = 10$ are calculated as follows:

$$\begin{aligned} \text{MVC} = & \frac{0.7(8[\text{ar. ether}] + 18.72[\text{ketone}] + 2 \times 65.5[\text{phenylene}])}{2 \times 0.3[\text{sulfonic acid group} \times \text{mole ratio}]} \\ & + \frac{0.3(8[\text{ar. ether}] + 18.72[\text{ketone}] + 2 \times 65.5[\text{phenylene}] + 2 \times 40.5[\text{sulfonic acid}])}{2 \times 0.3[\text{sulfonic acid group} \times \text{mole ratio}]} = 303.4 \end{aligned}$$

$$\text{PCV} = \frac{18.10}{303.4 + 18.10} = 0.372$$

Table 2 summarizes the properties of PEMs used for this study. Relative values for conductivity (σ), methanol permeability (P_M) and selectivity (Φ) versus Nafion® (EW = 1100, as reported in the literature references) are presented in order to reduce systematic errors derived from different test conditions (temperature, methanol concentration, etc.) and methodologies. While this approach still brings with it concerns (such as different temperature dependencies for various properties), it was deemed to be the “fairest” way to compare the large selection of data measured under different conditions. A wide range of properties of sulfonated PEMs has been covered based on molecular composition and polymer architecture. MVC values reported are in the range of 182–1498 ($\text{cm}^3/\text{mol.equiv. of acid groups}$); λ values from 0.8 to 55.5, PCV values from 0.05 to 0.78, σ from 0.003 to 2.09, P_M from 0.02 to 1.83 and Φ from 0.56 to 17.5. The range of Nafion values reported is the result of different EW samples. Many PEMs have selectivity more than twice as good as Nafion control (EW = 1100) and a few

PEMs have selectivity more than an order of magnitude higher than Nafion. The implications of high selectivity PEMs will be discussed later.

3.2. PCV analysis on proton conductivity and methanol permeability

Since DMFCs are typically operated under fully humidified conditions, liquid water equilibrated conductivity of a PEM should be a reasonable gauge of expected ohmic losses assuming that other factors such as electronic resistance, interfacial resistance, and conductivity dependence in the presence of methanol are minor. Fig. 1 shows the relative conductivity (σ) of various PEMs as a function of PCV under liquid water equilibrated conditions. Fig. 1 expands on previously reported data [6] and contains a modified legend based on the classification of PEMs we presented earlier. A strong correlation exists between proton conductivity in fully hydrated PEMs and PCV. Proton conductivity increases an order of magnitude as PCV increases from 0 to ~0.35 and then increases more slowly. In our previous investigation, we attributed the marginal increase of proton conductivity after PCV 0.35 to a dilution of sulfonic acid groups [6]. In this PCV range, PEMs exhibit excessive water uptake and their mechanical properties (ca. modulus and strength) deteriorate accordingly. As a result, most well-performing PEMs for H_2/air fuel cells have PCV values of ~0.35 where conductivity is relatively high (ca. 0.05–0.1 S/cm) while water uptake is moderate (ca. <60 wt.%). While the scatter of data on Fig. 1 is significant, conductivity is much better correlated with PCV than other parameters as we have previously shown [6], and correlates reasonably with a master curve (shown by the black dashed line). Having plotted the data as we have in Fig. 1, based on our arbitrary breakdown of polymer classes, we can access the potential role of polymer structure, often cited as a reason for significantly higher conductivities when comparing

different polymers. Somewhat surprisingly, Fig. 1 shows no strong trends between polymer families. These data show that proton conductivity for fully hydrated PEMs using the PCV parameter shows little dependence on polymer families and the differences in molecular structure and/or morphology that exist. This may be due to the incorporation of significant amounts of water (ca. $\lambda > 10$) in fully hydrated PEMs that diminishes the importance of structural and compositional characteristics through the formation of more continuous, less tortuous, higher water content, hydrophilic domains. It is worth noting that under partially humidified conditions, we observed stronger effects on proton conductivity [6].

Fig. 2 shows the relative methanol permeability (P_M) of various PEMs as a function of PCV. Methanol permeability increases as the PCV value increases without a definite slope transition. Unlike conductivity (as shown in Fig. 1) which showed an inflection at a PCV value of 0.35, methanol permeability does not suffer from a same dilution of sulfonic acid sites at high water contents and exhibits similar trends over the full PCV range presented. This is not surprising, because unlike proton conductivity which depends on sulfonic acid sites to provide the local protonic con-

Table 2Polymer classification, MVC, λ , PCV, relative conductivity (σ), methanol permeability (P_M) and selectivity (Φ).

Polymer	Category	MVC (cm ³ /equiv. mol.)	λ (H ₂ O/SO ₃ H)	PCV	σ	P_M	Φ	References
Nafion	PFSA	373–714	10.8–34.2	0.21–0.62	0.35–1.62	0.48–1.83	0.74–1.01	[8]
Nafion/poly(arylene ether ketone)		271–499	12.2–15.3	0.35–0.45	0.49–0.83	0.44–0.71	0.96–1.16	[9]
Nafion/silica		279–588	14.1–17.9	0.30–0.36	0.93–1.22	0.85–0.95	1.08–1.74	[10]
Nafion/poly(<i>p</i> -phenylene vinylene)		547–573	12.7–14.1	0.29–0.32	0.68–0.83	0.40–0.61	1.37–1.71	[11]
Nafion/fluorinated ethylene–propylene	Partially fluorinated	583–1498	6–18	0.06–0.36	0.03–0.68	0.03–0.67	0.57–5.42	[12]
Nafion/poly(1-vinylimidazole)		527–560	3–16	0.09–0.35	0.18–0.91	0.05–0.84	1.08–3.63	[13]
Fluorinated Poly(arylene ether)		499–721	10.6–14.2	0.21–0.34	0.12–0.64	0.10–0.48	0.69–3.72	[14,15]
Poly(arylene ether ketone)	Homo	437–487	7.6–9.8	0.22–0.29	0.64–1.09	0.15–0.21	4.31–5.13	[16]
Poly(arylene ether sulfone)		317–708	6.1–29	0.13–0.75	0.06–1.44	0.06–1.17	0.56–3.40	[17–22]
Poly(arylene ether ketone)		317–1225	9.2–27.2	0.13–0.59	0.09–1.22	0.03–1.00	0.61–6.92	[16,17,23–26]
Poly(phenylene)	Random	182–845	6.0–34.6	0.19–0.61	0.13–1.23	0.06–1.19	0.72–5.86	[27,28]
Polystyrene	HC based	335–336	17.6–27.2	0.49–0.59	0.57–0.78	0.73–1.00	0.77–0.88	[29]
Polyimide		221–904	6.8–24.9	0.19–0.55	0.004–1.09	0.04–0.47	1.71–4.63	[30–33]
Polystyrene		315–1465	8.1–55.5	0.34–0.46	0.01–0.89	0.30–0.71	0.70–14.33	[34,35]
Poly(arylene ether sulfone)	Multi-block	446–1349	20.5–36.4	0.33–0.57	0.45–2.09	0.02–0.55	2.67–5.00	[36,37]
Poly(arylene ether)		258–418	0.8–51.6	0.05–0.78	0.04–1.44	0.05–1.11	1.46–10.42	[38–41]
Polyimide	Cross-linked	221–517	6.7–14.5	0.31–0.39	0.69–1.24	0.10–0.34	3.62–9.75	[30]
Polybenzimidazole		254–1124	5.4–30.9	0.10–0.53	0.09–0.92	0.03–0.62	1.15–7.28	[42–47]
Polynitrile		396–513	8.1–10.3	0.26–0.31	0.60–0.78	0.23–0.42	2.36–3.52	[48]
Polyketone–amide		320–534	10.0–12.1	0.25–0.40	0.11–0.55	0.06–0.42	0.68–1.88	[49]
Polyketone–amine	Functional	396–486	6.5–7.7	0.19–0.26	0.25–0.88	0.11–0.38	1.82–2.21	[50]
Polyketone–carboxylic acid		230–973	14.2–20.6	0.13–0.55	0.003–1.25	0.02–1.25	1.15–17.5	[47,51,52]
Polysulfone–phosphine oxide		437–485	8.2–11.7	0.25–0.33	0.21–0.35	0.13–0.24	1.42–1.65	[53]

Fig. 1. Proton conductivity versus PCV of various sulfonated PEMs under fully hydrated conditions as a function of polymer category.

centration and where distances between these sites affect the rate at which protons pass, methanol as a neutral molecule is free to permeate without similar constraints. Additionally, Fig. 2 shows a clear trend of chemical/structural effects on methanol permeability. Again, unlike the conductivity data (Fig. 1), the methanol permeability data (Fig. 2) shows a clear trend based on polymer chemistry with decreasing methanol permeability in the order of PFSA > partially fluorinated > HC-based > functional PEMs. Blends of PFSA with methanol barrier polymers or additives (classified here as partially fluorinated PEMs) exhibit lower methanol permeability than PFSA at a given PCV, suggesting that using PFSA blends could improve DMFC performance over unmodified PFSA, while still having high methanol permeability compared to HC-based or functional PEMs. HC-based PEMs show lower methanol permeability than PFSA and partially fluorinated PEMs. Functional PEMs show the lowest methanol permeability. We have included cross-linked HC-based membranes as a separate subset in Fig. 2, as they were also found to have low methanol permeability. To date examples of functional PEMs with cross-linking have not been investigated in depth, but trends shown here suggest these materials would have very low methanol permeability.

Fig. 3 shows the relative selectivity (Φ) of various PEMs as a function of PCV. As selectivity is the ratio of conductivity to methanol permeability, it is of no surprise that some of the conclusions

Fig. 2. Relative methanol permeability P_M versus PCV of various sulfonated PEMs under fully hydrated conditions as a function of polymer category.

Fig. 3. Relative selectivity versus PCV of various sulfonated PEMs under fully hydrated conditions as a function of polymer category.

regarding Figs. 1 and 2 carry over to Fig. 3. Specific trends of relative selectivity based on molecular compositions are discernable and (inversely) consistent with trends reported for Fig. 2 (Functionalized > HC > Partially Fluorinated > PFSA). Still the data scatter appears larger for Fig. 3 than Fig. 2, and variability within specific polymer families (HC-based and functional PEMs) is increased. Still, the data presented here show clear trends and suggests that significant improvements in selectivity (compared to Nafion which has been the most commonly-used PEM for DMFC) are realizable. The relative selectivity plot shows a general trend that relative selectivity decreases as PCV increases. This could have been expected as the slope of methanol permeability dependence (Fig. 2) is greater than that of proton conductivity (Fig. 1). As a result, only a few highly selective PEMs are available at a high PCV range (e.g. only 2 out of 48 PEMs have selectivity of >4 at PCV of 0.4 or greater), and the most selective polymers have exceptionally low PCV. This suggests that PEMs having high PCV values (high degree of sulfonation and high water uptake) are less attractive for DMFC applications due to their low selectivity with the notable exception of PFSA's that are roughly independent of PCV value (ranging from 0.74 to 1.01) and have poor selectivity at all PCV.

In addition to low selectivity, PEMs having high PCV values have an increased disposition towards poor mechanical stability when incorporated into MEAs due to high water uptakes and large associated dimensional changes and resultant stresses. Failure points often result where these stresses are largest, in places such as at the edges of cell active area (where movement of the MEA is restricted and resist hydration) or at the membrane-electrode interfaces (where highly swollen PEMs are in contact with electrode layers). Fig. 4 shows trend of PCV versus water uptake for PEMs within three different PCV ranges. Although there is considerable distribution of water uptake within each of these three ranges and some overlap, a clear trend of increasing water uptake with increasing PCV is apparent and expected. These results are presented, because the ultimate limit of water uptake that might be tolerable for a durable MEA is likely limited. For example if water uptakes less than 50% were required, PCV values <0.55 would have to be targeted.

While high PCV PEMs are limited due to water uptake, low PCV PEMs have issues with low conductivity and the minimum thickness at which they can be used. While ohmic losses are less important for DMFCs than H_2 /air fuel cells as they tend to operate at lower current densities, ohmic losses will become important

Fig. 4. Water uptake distribution of sulfonated PEMs at a given PCV ranges.

as conductivity decreases substantially. For example, PEMs having PCV of ~0.2 only have on average about 20% of the conductivity of Nafion (1100 EW). DMFCs can also partially offset increased ohmic losses by decreased crossover rates and performance losses associated with mixed potential effects due to having methanol at the cathode. For optimized systems where methanol concentration is tuned to minimize crossover these gains are relatively modest [2]. PEM thickness can also be decreased up to a point. As several low PCV PEMs have high relative selectivity (Fig. 3), they can exhibit decreased methanol crossover even as thin membranes. However, mechanical stability of PEMs also decreases with thickness and handling and processing of thin PEMs can be extremely difficult. As a result, high performing DMFC PEMs have often been selected with PEMs having somewhat higher PCV (ca. ~0.35) in which comparable cell resistance to MEA using Nafion can be achieved with a reasonable thickness (ca. 30–60 μm) [22,54]. Highly selective but low PCV polymeric materials, on the other hand, are of potential interest and have been demonstrated as thin coating layers (ca. 1–10 μm) using less selective but highly conductive PEMs. In many cases compatibility of these layers may be an issue, but in at least

Fig. 5. Effect of degree of functionalization on methanol permeability illustrated by comparing methanol permeability of Nafion® [8] and PVI incorporated Nafion® [13].

one case, a composite PEM has shown superior DMFC performance and durability [55].

Polymers that contain functional moieties have been highlighted in our division of polymer classes and have shown favorable properties for DMFCs. Fig. 5, obtained from data taken from reference 13, illustrates the effect that a functional group (imidazole in this case) has on proton conductivity, methanol permeability and selectivity by comparing unmodified Nafion® [8] and Nafion®/poly(1-vinylimidazole) (PVI) blend [13]. The Nafion/PVI blend was prepared by impregnating different amounts of 1-vinylimidazole in a Nafion 112 membrane (EW=1100) and polymerizing to poly(1-vinylimidazole) (PVI) by UV irradiation. Proton conductivity of Nafion and the Nafion/PVI blend (Fig. 5a) are nearly identical at a given PCV value, consistent but much more stringent when compared with the results of Fig. 1. Methanol permeability of both Nafion and Nafion/PVI blend decrease as PCV decreases (Fig. 5b). However, unlike conductivity, the decrease of methanol permeability for Nafion/PVI blend at a given PCV is significant as PVI content increases. The trend in selectivity (Fig. 5c) reflects the combination of conductivity and methanol permeability (Fig. 5a and b). In this case, the functional group presented, imidazole, is basic

under the acidic conditions within Nafion. The acid-base interaction decreases the water uptake at a given sulfonation level thereby lowering the PCV value. Other functional groups may have different impacts, but the functional groups having specific interactions tend to decrease water uptake in general.

Beyond reducing water uptake, the structure of water domains through which transport occurs are almost certainly impacted, as well as perhaps PEM morphology. The state of water in PEMs is often probed and related to the properties discussed here: conductivity, methanol permeability and selectivity [27,56–58]. PEMs containing functional groups have decreased water uptakes and exhibit properties consistent with smaller water domains and less free water. Kim et al. observed the methanol permeability of PEMs is qualitatively proportion to the free water content, suggesting that the state of water is critical to methanol permeability [58]. Our PCV analysis suggests that conductivity is not as dependent on this parameter, and as a result functional PEMs appear promising for DMFC applications in terms of high selectivity. Cross-linked systems, which also have reduced water uptakes, show similar improvements in selectivity, likely for similar reasons.

3.3. Relationship between MVC, λ and P_M

In the previous section, proton conductivity, methanol permeability and selectivity of a wide range of PEMs were analyzed using the PCV parameter. The analysis presented suggests that PEMs having relatively low PCV values have the best potential for DMFC applications in terms of optimal selectivity, although conductivity and mechanical properties limit very low PCV PEMs. The averaged values of MVC and λ values of the categorized PEMs at a fixed PCV are listed in Table 3 to facilitate discussion about the detailed structural effect of PEMs. A PCV of 0.35 was chosen as an intermediate PCV value for further study. A decreasing trend of methanol permeability (i.e. PFSA > partially fluorinated > HC-based > functional PEMs $\approx$ cross-linking) and increasing selectivity within the categorized molecular composition is consistent with the trends presented earlier, for PEMs over the whole range of PCV values. MVC and λ decrease as the molecular composition changed from PFSA to HC-based to functional PEMs and finally to cross-linked PEMs. Assuming that the conductivities of PEMs are similar at a given PCV, this indicates that the conductivity of PFSA and partially fluorinated PEMs is obtained at a relatively low sulfonic acid volume concentration (i.e. high MVC) and high water content (i.e. high λ) at a given PCV. In contrast, similar conductivity was obtained with HC-based, functional and cross-linked PEMs where the sulfonic acid volume concentration is high (i.e. low MVC) and with a low water content (i.e. low λ). Although one should not assume that a single λ value can be used for quantitative estimation of methanol permeability, because the difference in dielectric constants, partition coefficients, tortuosity, and the distribution of states of water were not taken into, trends between methanol permeability and the combination of MVC and water holding capacity of each of the categorized PEM systems at a fixed PCV are evident.

The same analogy regarding the relationships between MVC, λ , and P_M can be applied within categories of HC-based and functional PEMs. Table 4 shows the MVC and λ of HC-based and functional PEMs at PCV of ~ 0.3 . The methanol permeability varied significantly within the HC-based and functional PEM categories depending on the detailed molecular structure and specific interaction. Among the HC-based PEMs, a PEM with bromo-phenylene oxide backbone structure exhibited unusually low MVC and λ . This is probably due to the hydrophobic nature of bromine which effectively reduces water uptake without specific interactions. While all functional PEMs exhibit effectively reduced methanol permeability by decreasing MVC and λ , the PEMs with high dipole interac-

Table 3

Average values of MVC, λ , PCV, relative conductivity (σ), methanol permeability (P_M) and selectivity (Φ) for PEMs (PCV=0.35). Numbers in the parenthesis denote the standard deviation.

PEMs	No. data	PCV	MVC (cm ³ /equiv. mol.)	λ (H ₂ O/SO ₃ H)	σ	P_M	Φ
PFSA	3	0.35 (0.03)	550 (40)	16.5 (1.8)	0.85 (0.18)	0.88 (0.11)	0.9 (0.1)
Partially fluorinated	11	0.35 (0.02)	531 (73)	15.9 (2.0)	0.87 (0.23)	0.73 (0.16)	1.2 (0.2)
HC-based	12	0.35 (0.01)	459 (85)	13.7 (2.3)	0.86 (0.24)	0.35 (0.12)	2.5 (1.0)
Functional	14	0.35 (0.03)	407 (83)	12.5 (3.2)	0.83 (0.33)	0.24 (0.12)	5.1 (3.5)
Cross-linked	12	0.35 (0.02)	397 (45)	11.6 (2.4)	0.98 (0.18)	0.21 (0.06)	6.3 (2.5)

tions such as phosphine oxide or amide have a more profound effect than those with low specific interactions such as nitrile or carboxylic acid groups. For example, the PEM with 2 vol.% phosphine oxide group has MVC and λ of 440 (cm³/equiv. mol.) and 9.6 (nH₂O/SO₃H), respectively while the PEM with 8 vol.% nitrile group has a greater MVC and λ of 493 (cm³/equiv. mol.) and 12.2 (nH₂O/SO₃H). High dipole interactions may also impact the proton conductivity as the proton conductivity of these functional PEMs is noticeably lower than other functional PEMs. This is not readily apparent in Fig. 1 and Table 2, but it appears as slightly lower conductivity with greater data scattering for functional PEMs. This result suggests that strong dipole interactions, particularly with sulfonic acid groups, may not be desirable for DMFC PEMs. However, it is hard to draw conclusions from our current data as to what types of functional groups are more effective for methanol blocking, due to the difficulties of normalizing the volume fraction of functional groups, polymer architecture difference, and lack of available statistical data.

Polymer architecture also impacts the methanol permeability. Table 5 shows the MVC, λ and PCV values for HC-based cross-linked, homo, random, and multi-block (co) polymers. Comparison of these PEMs at PCV of 0.25 shows a clear trend that MVC and λ increase in the order of cross-linked copolymer, homopolymer and random copolymer (MVC increased from 328 to 638, and λ increased from 5.6 to 12.0). Relative methanol permeability increased accordingly from 0.16 to 0.19. Multi-block copolymer shows higher MVC and λ values than random and cross-linked copolymers when compared at PCV of 0.42. This result suggests that lower methanol permeability is expected with cross-linked copolymers and homopolymer-like structures compared to uncross-linked random copolymers and these would possibly have lower methanol permeability than multi-block copolymers. Unlike some functional PEMs, conductivity reduction due to cross-linking was not observed, which results in cross-linked PEMs having excellent selectivity. Although the availability of PEM data having different polymer architectures is somewhat limited to generate statistical data, this result indicates the importance of polymer architecture in addition to molecular composition of sulfonated polymers on methanol barrier properties.

3.4. Molecular design and optimization of DMFC PEMs

Conventionally, adjusting PEM properties for DMFC applications has been achieved by controlling IEC (or degree of sulfonation) of PEMs having same molecular structure. This approach provides a relatively easy way to manipulate PCV. However the selectivity of the PEMs is determined where the PCV is obtained. For blend PEMs, often a base PEM with a fixed IEC was selected and mixed with the other component, which normally has a methanol barrier property of a different ratio. In this case, the selectivity of PEM may be improved, but it is hard to control PCV in a systematic way since MVC and λ of the blend PEMs are affected by composition of the blend PEMs. Our results suggest changing molecular composition and polymer architecture can greatly improve the PEM properties and therefore, it is of interest to know the practical methodology to obtain optimized PEMs.

Fig. 6 shows a schematic illustration of optimization process of PEMs by incorporation of functional groups or cross-linking. Data from non-crosslinked and cross-linked sulfonated poly(arylene ether sulfone) random copolymers [22,59] were used for the illustration, but this strategy can be used for both PFSA and HC-based PEMs. Fig. 6a shows the λ in a log scale as a function of IEC. In many cases, three regimes are discernible depending on water holding capability recognized by the slope of λ : (i) Regime 1 (R1): before the percolation threshold of hydrophilic domains; (ii) Regime 2 (R2): after the percolation threshold of hydrophilic domains; and (iii) Regime 3 (R3): after hydro-gel formation. Typical well-performing PEMs for DMFC applications are located at the percolation threshold (denoted as a filled square), where PCV approaches 0.35. Fig. 6b shows the log scale equivalent wet volume per sulfonic acid groups (i.e. MVC_(WET)) as a function of IEC. A minimum value is obtained at the transition of R1 and R2 (percolation threshold) where dilution due to excessive water starts to increase the volume between sulfonic acid groups. The λ in Fig. 6a to MVC_(WET) in Fig. 6b convert from the mass scale parameter, IEC to the length scale parameter, PCV. Fig. 6c and d show the proton conductivity and methanol permeability in a log scale as a function of PCV, respectively. The conductivity increases rapidly through R1 and slows down in R2 and falls in R3, while the methanol permeability increases with PCV in a linear pattern, as observed in Figs. 1 and 2. With func-

Table 4

MVC, λ , PCV relative conductivity (σ), methanol permeability (P_M) and selectivity (Φ) of HC-based and functional PEMs (PCV = 0.30).

Functional group (backbone)	Vol.%	PCV	MVC (cm ³ /equiv. mol.)	λ (H ₂ O/SO ₃ H)	σ	P_M	Φ	Ref.
None (phenylene)	0	0.29	618	14.3	0.49	0.40	1.2	[27]
None (ketone-sulfone)	0	0.29	560	12.9	0.36	0.28	1.3	[23]
None (sulfone-imide)	0	0.30	554	13.1	0.36	0.24	1.5	[32]
None (sulfone)	0	0.31	475	11.9	0.51	0.19	2.7	[19]
None (bromo-phenylene)	0	0.29	252	5.5	0.33	0.08	4.2	[28]
Carboxylic acid (ketone)	5	0.31	518	12.6	0.36	0.20	1.8	[47]
Nitrile (phenylene)	8	0.31	493	12.2	0.84	0.24	3.5	[48]
Amide (ketone)	4	0.32	408	10.5	0.19	0.18	1.0	[49]
Phosphine oxide (sulfone)	2	0.28	440	9.6	0.26	0.16	1.7	[53]
Imidazole (sulfone)	14	0.28	441	9.1	0.43	0.10	4.3	[44]

Table 5
MVC, λ , PCV, relative conductivity (σ), methanol permeability (P_M) and selectivity (Φ) of HC-based homopolymers, random copolymers, multi-block copolymers and cross-linked copolymer (PCV = 0.25 and 0.42).

Polymer architecture	No. data	PCV	MVC (cm ³ /equiv. mol.)	λ (H ₂ O/SO ₃ H)	σ	P_M	Φ	Ref.
Cross-linked copolymer	3	0.25 (0.06)	328 (67)	5.6 (1.7)	0.66 (0.2)	0.16 (0.04)	6.3 (3.8)	[38–41]
Homopolymer	2	0.25 (0.05)	462 (35)	8.7 (1.5)	0.39 (0.1)	0.18 (0.05)	4.7 (0.6)	[16]
Random copolymer	6	0.26 (0.03)	638 (75)	12.0 (1.9)	0.46 (0.2)	0.19 (0.08)	2.6 (1.0)	From Fig. 2
Cross-linked copolymer	6	0.42 (0.06)	337 (69)	13.8 (4.0)	1.00 (0.3)	0.27 (0.12)	4.1 (1.4)	[38–41]
Random copolymer	4	0.41 (0.01)	458 (95)	18.0 (3.6)	1.00 (0.3)	0.30 (0.03)	3.3 (0.9)	From Fig. 2
Multi-block copolymer ^a	2	0.42 (0.01)	574 (8)	23.0 (0.7)	0.92 (0.1)	0.32 (0.01)	2.9 (0.3)	[37]

^aNafion® data was taken from Ref. [36] since no Nafion data was provided from Ref. [37].

tionalization (or cross-linking) of a PEM in R3 (i.e. in the hydro-gel state), λ can be reduced significantly (unfilled to filled star in Fig. 6a) to a similar level of the un-modified PEM at percolation threshold (filled square). Correspondingly, MVC_(WET) decreases without changing IEC (Fig. 6b). The PCV value then is slightly decreased as λ decreased. The conductivity is traced back accordingly (Fig. 6c). The conductivity change in the PCV range over 0.35 is not significant as it appears in Fig. 1. Now the functionalized PEM (filled stars) have lower λ and MVC when compared with the un-modified

PEM (filled squares) at the same PCV. The functionalized PEMs have comparable conductivity (due to the similar PCV) to and lower methanol permeability (due to the lower λ and MVC values) than un-modified PEMs (filled square). In summary, the incorporation of functional groups or cross-linking can effectively lower methanol permeability (Fig. 4d) by decreasing λ and MVC while maintaining proton conductivity. Due to their lower water uptake, a similar level of improvements in mechanical properties can also be expected.

Fig. 6. Schematic illustration of optimization process for DMFC PEM; property changes upon polymer modifications (a) hydration number (λ), MVC + 18 λ , (c) conductivity, and (d) P_M ; Filled square: optimum PEM without modification (determined by percolation threshold); unfilled star: PEM properties before functionalization (or cross-linking); filled star: PEM properties after optimization.

Polymer molecular design such as non-fluorinated polymers, those containing certain functional groups, and changing polymer architecture have been shown to generally improve PEM properties for DMFC. The push towards preparing advanced PEMs using these strategies sometimes requires high levels of sulfonation, high degrees of functionalization and/or cross-linking, and special polymerization techniques, which often produce less flexible and mechanically poor PEMs. Incorporation of certain bulky functional groups or cross-linking which provide PEMs with sufficiently high sulfonation levels in order to attain optimum PCV can be problematic. Indeed, a few highly sulfonated, functionalized, and/or cross-linked polymers may not have sufficiently good mechanical properties to allow them to operate under sustained longer term fuel cell operations [54]. Therefore, the incorporation of flexible chain linkages into the PEM structure may be considered as a viable strategy to enhance mechanical properties, providing they have sufficient inherent stability. Another consideration is the optimization of the membrane-electrode assembly (MEA) fabrication in order to reflect the PEM properties on DMFC performance. Membrane-electrode interfacial failure, in particular, is often observed when hydrocarbon-based polymers are almost universally coupled with PFSA-bonded electrodes. Although this is outside the scope of this paper, there are a few references in this regard [60,61]. Improved DMFC performance is then anticipated with a well-designed DMFC PEMs [62,63].

4. Conclusions

Proton conductivity and methanol permeability of a wide range of sulfonated PEMs were analyzed using length scale parameters for DMFC applications. While proton conductivity was controlled by the single PCV parameter, methanol permeability substantially increased with water uptake (expressed by λ). Therefore, desirable properties are obtained with high volume sulfonic acid concentration (expressed by MVC) and low water uptake (expressed by λ). These facts described above provide some insights regarding the design or optimization of advanced DMFC PEMs from the molecular composition and architectural aspects: (i) absence of fluorine in PEMs can significantly improve PEM properties for DMFC. Although replacing hydrogen with fluorine increases volume sulfonic acid concentration (and thus conductivity), the fluorination cannot adequately compensate high methanol permeability derived from larger water domain structures. (ii) Methanol barrier properties of HC-based PEMs can be significantly improved by changing polymer molecular structure or introducing hydrophobic substituent. (iii) Incorporation of functional groups may also improve PEM properties. Functional groups having strong dipole interactions effectively reduce the MVC and water uptake. However, these often reduce proton conductivity due to their strong interaction with sulfonic acid groups, producing relatively moderate increases in selectivity. Another issue with functional groups having strong dipole interactions is the composition range for incorporation is very narrow. In this case, it requires very precise control of incorporation of the functional group. On the other hand, functional groups with relatively weak dipolar interactions such as nitrile group can provide a relatively broader compositional window and uniformity. (iv) Changing polymer architecture to homo-polymer like structure from random or multi-block copolymers may improve methanol barrier properties. Cross-linking is more aggressive way to improve methanol blocking properties, although significant reduction of MVC and λ are typically expected. Like the PEMs with strong specific interaction, the compositional window for cross-linking is narrow and thus, low levels of cross-linking may be desirable to obtain good PEM properties. Although detailed optimization for specific polymer systems is still needed, this paper provides gen-

eral directions and insights for the design of advanced DMFC PEMs, which can be implemented into any specific system.

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